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ON TAR SAND AND HEAVY OIL

CHARACTERIZATION OF OIL SAND RESOURCES

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CHARACTERIZATION OF OIL SAND RESOURCES

REPORT ON THE ACTIVITIES CONCERNING ANNEX 1 OF THE U.S.-CANADA COOPERATIVE AGREEMENT ON TAR SAND AND HEAVY OIL

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CHARACTERIZATION OF OIL SAND RESOURCES

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April 1988

FOREWORD

Since 1979, the Canadian Department of Energy Mines and Resources (CANMET), the United States Department of Energy, Saskatchewan Energy and Mines, and the Alberta Oil Sands Technology and Research Authority have participated in a Memorandum of Understanding. The purpose of this cooperation agreement is to encourage the development and exchange of U.S. and Canadian technical information on oil sands and heavy oil.

This report is the third published under this cooperation agreement. It summarizes and discusses an extended and arduous effort on the part of the U.S. and Canadian analytical laboratory researchers to develop the technical basis for reliable, comparable measurement of physical and chemical properties of oil sands (tar sands). The conclusion reached by the participating experts from the Western Research Institute (Laramie, Wyoming) and the Alberta Research Council (Edmonton, Alberta) was that general agreement in property measurement technique can be had, with the exception of asphaltenes, which were found unique to their respective bitumen. This general accord in analytical approach is indeed welcome to the sponsors of this work and, hopefully, will facilitate the task of energy resource assessment within our two countries.

This work was sponsored by the United States Department of Energy (Fossil Energy) and the Alberta Oil Sands Technology and Research Authority (AOSTRA) under the auspices of the U.S./Canada Memorandum of Understanding for cooperation in the research and development of oil sands and heavy oil.

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SUMMARY

Under the terms of Annex I of the U.S.-Canada Cooperative Agreement on Tar Sand and Heavy Oil the organizational and laboratory work leading to the development of a physical properties data base has been completed. The data base will be a vehicle for the transfer of information about tar sand and heavy oil between participants of the agreement and to the public.

Information required for complete geological and engineering descriptions of tar sand and heavy oil deposits has been identified. Geological descriptions of the Athabasca and Asphalt Ridge deposits have been prepared. However, little information about many of the engineering properties, such as magnitude and direction of minimum and maximum permeabilities, is available in the literature. The data base will, in its early stages, contain little engineering data.

A computerized data base, developed at the Alberta Research Council, includes information on the visual examination of whole oil sand and determination of physical and chemical properties of whole oil sand and bitumen. Data from cooperative studies sponsored by the Alberta Committee on Oil Sands Analysis and the Phillips Petroleum Company were used to estimate the precision of data in the open literature that would be entered into the data base. These studies showed that systematic errors during analysis (i.e. lack of agreement between laboratories for properties of a single sample) will seriously diminish the significance of a single data point in the data base. This type of data can best be used to estimate the typical properties of a deposit.

In an attempt to identify some of the reasons for variations in analytical data and to resolve discrepancies, the Western Research Institute and the Alberta Research Council exchanged samples of oil sand from the Asphalt Ridge and Athabasca deposits. They were able to provide equivalent data for most properties, the exceptions being elemental carbon, carbon residue, relative density (15°C/15°C), and C_5-asphaltenes. A difference in methods for extracting test samples of bitumen was identified as being a potential contributor to differences in the bitumen properties.

In subsequent studies at the Alberta Research Council, failure to correct for entrained solids and residual solvent, which was related to sample preparation, was confirmed to be a major source of discrepancy between the two laboratories' data. In addition, the level of asphaltenes was significantly affected by prolonged exposure to heat and selective adsorption on cellulose thimbles in the extraction apparatus.

A final exchange of bitumen samples prepared at the Alberta Research Council indicated that discrepancies changed with the capabilities of the laboratories. It appears that the systematic errors that contribute to these discrepancies can only be controlled or at least minimized through the use of secondary standards.

1. INTRODUCTION

1.1 Incentives

On June 4, 1979, the United States Department of Energy, the Alberta Oil Sands Technology and Research Authority, the Department of Energy, Mines and Resources of Canada, and the Department of Mineral Resources of the Province of Saskatchewan signed an agreement entitled "Memorandum of Understanding for Cooperation in the Research and Development of Tar Sands (Oil Sands) and Heavy Oil." The memorandum identified six projects that are related to research and development of tar sands and heavy oil and in which the signatories agreed to cooperate. The projects were:

- parametric analyses of tar sand and heavy oil characteristics (Annex 1)
- comparative economics and sweep efficiencies of steam flooding and in situ combustion methods
- permeability enhancement methods
- treatment and use of water produced during tar sand and heavy oil development
- steam flooding with additives (Annex 2)
- shaft and tunneling design; laboratory and field project review

Annex 1 was organized under a proposal entitled "Joint Canadian-U.S. Proposal for Resource Characterization of Oil Sands (Tar Sands)." The following objectives were established:

- Assemble, coordinate, and interpret existing knowledge of the U.S. and Canadian resources and the characteristics of each deposit.
- Develop comprehensive data on the nature of major oil sand deposits. The choice of recovery and upgrading methods for a deposit is governed by its geological and engineering properties and the physical and chemical properties of the oil. A data base that describes each deposit in these terms would eliminate some of the alternatives that would otherwise be considered in the development of a resource.
- Develop an oil sand resource and deposit characteristics data base employing computerized methods and, thus, facilitate the transfer of oil sand information to the public and to each other's data base.

The objectives could be met by:

- defining the geological and engineering characteristics that should be reported to completely characterize a deposit
- defining the petrological, physical, and chemical characteristics that would completely characterize a particular tar sand sample
- ensuring concurrence of analytical measurements conducted on samples of tar sand by participation in interlaboratory sample exchanges
- compiling existing data on U.S. and Canadian tar sands deposits
- establishing central physical property data bases in the United States and Canada through which information could be exchanged

This report describes work carried out by the Western Research Institute (WRI) in Laramie, Wyoming, and the Alberta Research Council (ARC) in Edmonton, Alberta, to meet the objectives of Annex 1.

1.2 Work Plan

The strategy to develop a reliable data base entailed several distinct stages.

Definition of Parameters: Geologists, chemists, and petroleum engineers from ARC, WRI, and the Department of Energy, Mines and Resources of Canada prepared a list in February 1980 of the elements that should be included in a complete characterization of a deposit. These are detailed in Chapter 2.

Ensuring Concurrence of Analytical Data: WRI and ARC exchanged samples of Athabasca and Asphalt Ridge tar sands to determine if equivalent physical and chemical information would be reported by the two organizations for identical samples of tar sand (Chapter 4). Accepted quality assurance/quality control procedures were followed at both laboratories. ARC conducted further studies to reconcile potential differences between the two sets of data (Chapter 5). In addition, both organizations participated in sample exchanges, apart from those specified in Annex 1, to compare their capabilities with other laboratories and to assess the variability in analytical data that is generated in the United States and Canada (Chapter 3). The Alberta Committee on Oil Sands Analysis and the Phillips Petroleum Company in Bartlesville, Oklahoma, sponsored cooperative exchanges. The data from these studies were key considerations in the evaluation of the concept of the data base.

Compilation of Data: Existing data in the literature were collected. The variability in the collected data was compared with the analytical variability of the results of many laboratories analyzing a common sample. If the analytical variability was relatively small, a high level of confidence could be placed on single data points in the data base. Unfortunately, the analytical variability was not small (Chapter 3).

Development of Data Base Software: A computerized data base was developed that permits exchange of information between the U.S. and Canadian centers and allows searching by terms such as country, field, or specific physical or chemical property.

2. CHARACTERIZATION OF AN OIL SAND DEPOSIT

2.1 Background

The characterization of a deposit is an evolutionary process starting with the examination of a single sample. As the analyses of more samples are reported, descriptions of deposits become more complete. A description in the form of a brief outline with a list of references attached has the flexibility to permit the addition of new data. The information needed for a data base follows.

2.2 Geological Description

Some of the elements listed below are addressed in the normal course of a preliminary coring program, but a complete geological description of a deposit will emerge only in the course of extensive field studies.

A geological description includes definition of

- geological setting: regional stratigraphy, depositional paleogeography and structural geology (e.g. folding, faulting)
- thickness and nature of oil-bearing zone; thickness of host formation; gross pay thickness; net pay thickness; lithology of host rock
- areal extent of oil-bearing zones
- reservoir continuity: facies patterns (geometry of reservoir sand bodies relative to associated tight zones) normally including compositional interpretation of the depositional environments
- distribution, degree, and nature of fluid saturations in gross pay zone and immediately adjacent zones
- thickness and character of the overburden and underlying strata
- hydrology: regional and local formation water flow patterns

Geological descriptions of the Athabasca and Asphalt Ridge deposits are attached as Appendices A and B.

2.3 Engineering Description

The following elements are needed for an engineering evaluation of a reservoir before a recovery process is selected. At present, many of these parameters cannot be determined either in the field or in the laboratory so estimates must be made on the basis of related data. Little information about many of these properties is available in the literature.

- saturations at reservoir conditions: oil, water, free gas
- porosity at reservoir conditions
- permeability: magnitude and direction of minimum and maximum permeabilities
- oil viscosity at reservoir conditions
- gas-oil ratio: flash and differential
- system wettability: capillary pressure, contact angle, interfacial tension
- salinity of formation water
- thermal conductivity
- electrical resistivity
- compressibility: solids, fluids
- degree of consolidation
- bulk density
- in situ stress field (for predicting fracture orientation)

2.4 Sample Description

The following characterizations are recommended for individual samples:

Visual Description

- principal lithology: color, grain size and sorting, major minerals and accessories, bedding characteristics, sedimentary structures, and other geological features
- estimates of oil saturation, porosity, and induration

Petrological Description

- grain-size distribution including sieve analysis to 325 mesh and fines distribution
- mineralogy: bulk and fines mineralogy, identification of heavy minerals
- other observations: cements (type, form, and amount of cement), rounding and sphericity, and pore shapes

Fluids

Special precautions should be taken in obtaining fluid samples for the following analyses in order to ensure correspondence with reservoir conditions:

- water: saturation, pH, conductivity, dissolved salts
- gases: saturation, composition
- liquid hydrocarbons: saturation, elemental composition (C,H,N,O,S), viscosity and density as functions of temperature and pressure, pour point, distillation range, functional groups and hydrocarbon types, trace metals, molecular weight, carbon residue

A typical description of a single sample from the Athabasca deposit is attached as Appendix C.

3. EVALUATION OF EXISTING CAPABILITIES FOR ANALYZING BITUMEN AND HEAVY OIL

3.1 Background

The variability in physical and chemical properties of bitumen as well as the diversity of facies and engineering properties within even limited areas of a deposit require that many samples must be analyzed before an adequate description of a deposit can be completed. The expense of analyzing a single sample and the problem of gaining access, which is often restricted to lease holders, make it unlikely that data for the data base will be collected by one organization as a stand-alone project. Therefore, data will have to be collected from the open literature and through the cooperation of lease holders.

Variations in data, however, exist even when a single homogenized sample is analyzed by several laboratories. Under such circumstances, it is difficult to distinguish between variations caused by analytical technique and those caused by the range of samples found in each deposit. This chapter describes the magnitude of depositional variability and analytical error.

3.2 Results of Cooperative Studies

In the past five years, two major cooperative studies have been carried out to determine the repeatability and reproducibility of analytical methods currently used to describe bitumen and heavy oil. In a cooperative study organized by the Alberta Committee on Oil Sands Analysis (ACOSA), samples of an Athabasca bitumen and a Lloydminster heavy oil were analyzed by 27 laboratories.[1] Forty-eight laboratories analyzed samples of a California and a Maya crude in a cooperative study sponsored by the Phillips Petroleum Co. of Bartlesville, OK.[2] Not all laboratories conducted all analyses on the samples but sufficient data were collected for each property to permit comparison of the precision of the data with precision standards developed by ASTM subcommittees for conventional crudes and refined petroleum products.

The within-laboratory precision (repeatability) for most properties in both studies was within ASTM repeatability standards. However, variations between laboratories were usually greater than ASTM reproducibility standards. The two-sample plots for nitrogen determations from both studies, shown as Figures 1a and 1b, illustrate the scale of between-laboratory variations. In a two-sample plot, the origin is located at the mean value found for each sample. Each laboratory's results are plotted in relation to the origin. With few exceptions, the data in the two-sample plots generated from both cooperative studies exhibited clear trends from the lower left to the upper right quadrant. This pattern arises from systematic differences between laboratories rather than random within-laboratory errors. It is usually found in data from cooperative studies regardless of the type of material being analyzed.

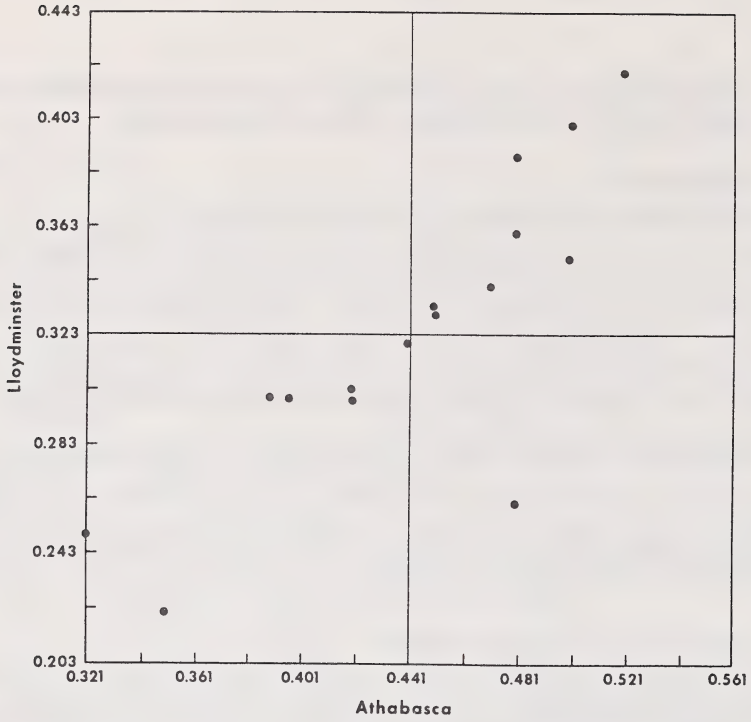


Figure 1a **Two-Sample Plot for Percentage of Nitrogen from the ACOSA Cooperative Study**

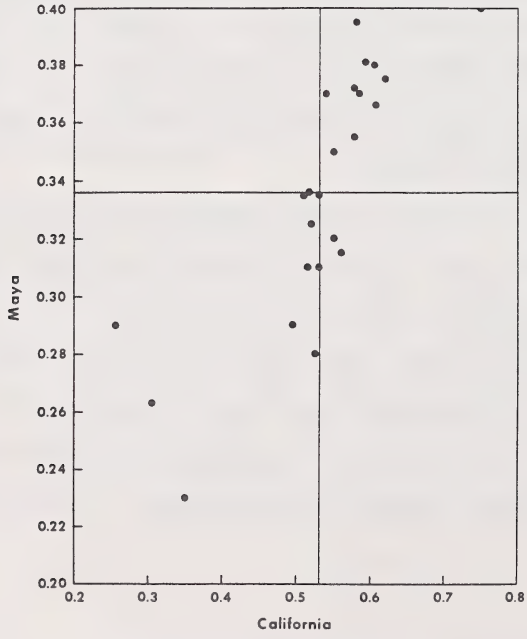


Figure 1b **Two-Sample Plot for Percentage of Nitrogen from the Phillips Cooperative Study**

The question to be addressed here is, are the systematic errors present during the analysis of well-defined bitumen and heavy oil samples large enough to obscure real differences between samples when data are provided by more than one laboratory?

In Table 1 the ranges are listed for many properties of a well-mixed sample of Athabasca bitumen analyzed by the laboratories participating in the ACOSA cooperative study of 1982.[1] For this comparison, no outliers were rejected. Outliers are difficult to identify when data are collected from the literature because there is no means of identifying data that are analytically incorrect. The ranges in Table 1 are usually larger for the single sample analyzed by several laboratories than the ranges reported by one laboratory for five samples.[3] These five samples represented the vertical profile of the Athabasca deposit on one lease.[4] The ranges from the ACOSA studies are from 31 to 246% of the range in values reported by numerous authors in the open literature for samples of Athabasca bitumen from many sites in the deposit. Comparison of the between-laboratory variability for Athabasca bitumen with that for Lloydminster, California, and Maya heavy oils (Table 2) reveals a remarkable similarity in the magnitude of systematic error. Data in this table do not include outliers that were identified by statistical tests.

These observations suggest that collection of data from a variety of sources will provide a reasonable estimate of the mean value for a deposit because an individual laboratory's bias will be offset by results of other laboratories. Little confidence, however, can be placed in the accuracy of the individual results, so the results from different laboratories cannot be used as a measure of variability of the deposit. On the other hand, analyses by a single laboratory will identify variability but there is no guarantee that the results will be accurate.

The plan to ensure that analytical data from the Western Research Institute and the Alberta Research Council are comparable is described in subsequent chapters. These organizations presumably would contribute only a small proportion of the data to the data base, so this effort must be expanded to include all contributing laboratories.

A thorough review of methods used to analyze bitumen and heavy oil is currently being compiled by ACOSA. One of the results of the review should be the identification of methods that are appropriate for analysis of bitumen and heavy oil. Certification of primary reference standards of bitumen will, however, be the most useful approach to reducing systematic error. This, too, is a long-term goal of ACOSA.

Table 1. Comparison of Ranges in Data Between Laboratories for One Sample and Between Samples from the Athabasca Deposit

	Range Between Laboratories – One Sample of Athabasca Bitumen[1] (*A*)	Range Between Five Samples of Athabasca Bitumen – One Laboratory[3]	Literature Values from Different Samples[4] (*B*)	Range of *A* x 100% / Range of *B*
Carbon (%)	82.13-83.84	82.96-83.88	81.9-84.63 (20)[a]	62.6
Hydrogen (%)	10.02-11.02	10.22-10.60	9.5-11.59 (21)	47.8
Nitrogen (%)	0.15-1.38	0.43-0.69	0.2-0.7 (21)	246
Sulfur (%)	3.19-6.20	4.20-4.66	1.11-5.6 (12)	67.3
Average Mole. Wt. (daltons)	426-576	521-605	319-800 (17)	31.2
Relative Density (15°C/15°C)	0.992-1.012	1.005-1.015	0.999-1.034	57.1
Asphaltenes (%)	9.7-17.1	15.9-18.2	9.3-22.5 (19)	56.1
Carbon Residue (%)				
CCR	12.02-14.66	–	9.8-18.5 (4)	31.0
RCR	9.0 -12.64	12.0-13.7	7.9-13.7 (14)	62.1
Metals (mg/kg)				
Nickel	17-86.8	66-81	30-112 (20)	85.1
Vanadium	174-306	192-211	112.1-290 (19)	74.2

[a]The number of values from the literature are given in parentheses.

Table 2. Comparison of Ranges in Data Between Laboratories for Samples Analyzed in Cooperative Studies

	ACOSA Study #1 Athabasca			ACOSA Study #2 Athabasca			ACOSA Study #2 Lloydminster			ACOSA Study #2 California			Phillips Study Maya		
	Min.	Max.	Range	Min.	Max.	Range	Min.	Max.	Range	Min.	Max.	Range	Min.	Max.	Range
Carbon (%)	82.93	83.5	0.57	82.13	83.84	1.71	82.16	84.31	2.15	83.05	84.35	1.30	83.65	85.40	1.78
Hydrogen (%)	9.94	11.47	1.53	10.02	11.02	1.00	10.46	11.53	1.07	11.20	12.13	0.93	10.95	11.66	0.71
Nitrogen (%)	0.39	0.54	0.15	0.32	0.52	0.20	0.22	0.42	0.20	0.51	0.65	0.14	0.31	0.40	0.09
Oxygen (%)	<0.8	1.0	>0.2	0.32	1.26	0.94	0.45	1.35	0.90	--	--	--	--	--	--
Sulfur (%)	4.10	4.98	0.88	4.27	6.20	1.93	3.43	5.01	1.58	3.00	3.75	0.75	2.80	3.52	0.72
Average Mole. Wt. (daltons)	393	522	129	426	576	150	351	549	198	--	--	--	--	--	--
Relative Density (15°C/15°C)	0.995	1.007	0.012	0.9917	1.0121	0.0204	0.9691	0.9749	0.0058	0.9396	0.9459	0.0063	0.9396	0.9455	0.0059
Viscosity[a] (cp)															
25°C	--	--	--	30299	42139	11840	2249	3058	809	269	308.5	39.5	150	167.5	17.5
60°C	--	--	--	1010.7	1519	508.3	179.68	262	83.32	131	149.6	18.6	81.1	107.4	26.3
100°C	81.3	113.4	32.1	111.5	130.3	18.8	34.42	52.3	17.88	77.3	91.2	13.9	52.1	75.6	23.3
Asphaltenes (%)															
C_5	--	--	--	13.66	17.1	3.33	11.41	14.5	3.09	12.00	14.85	2.85	12.48	14.38	1.90
C_7	--	--	--	9.67	10.0	0.33	7.15	9.86	2.71	--	--	--	--	--	--
Carbon Residue (%)															
RCR	10.57	11.9	1.33	8.5	12.18	3.68	5.2	10.62	5.42	8.45	9.58	1.13	10.20	11.22	1.02
CCR	10.91	12.38	1.47	11.5	14.21	2.71	9.09	11.54	2.45	8.95	9.98	1.03	10.80	11.90	1.10
Metals (mg/kg)															
Nickel	63	75.97	12.97	63	86.8	23.8	45.7	66	20.3	67.5	100.59	33.09	45	64.9	19.9
Vanadium	150	199	49	174	306	132	74.3	159	84.7	174.5	245	70.5	202	358	156

[a]In the Phillips round robin, viscosities were measured at 34°C, 65°C, and 100°C.

4. COMPARISON OF ANALYTICAL DATA FROM THE WESTERN RESEARCH INSTITUTE AND THE ALBERTA RESEARCH COUNCIL

4.1 Background

As shown in the preceding chapter, many variations in results can be attributed to differences in analytical technique among laboratories. The inter-laboratory variations need to be reduced if any confidence can be placed in the properties reported for a single sample in a data base. The Western Research Institute and the Alberta Research Council participated in three exchanges over a five-year period with the goal of comparing analytical data and resolving consistent differences.

4.2 Cooperative Studies

In addition to the work under the terms of the U.S.-Canada Agreement, the two laboratories participated in the ACOSA cooperative study in 1981 and the Phillips cooperative study in 1984 (described in Chapter 3). Comparisons of the elemental composition and relative density data from both studies are contained in Table 3. Close agreement is observed between the two laboratories for the ACOSA study for percentages of carbon, hydrogen, and sulfur. For example, 3.6% is the largest relative percentage difference between the two laboratories (sulfur determination for Lloydminster). However, the relative percentage difference between the two laboratories for determining nitrogen is very large, ranging from 14.4 to 24.0%. Three years later good agreement between the laboratories was obtained for the determination of carbon, hydrogen, and nitrogen. This time the relative percentage difference between the two laboratories for the determination of sulfur was large, ranging from 15.8 to 24.6%. The relative percentage difference between the two laboratories for the determination of relative density was 0.3% or less for both cooperative studies.

Table 3. Comparison of WRI and ARC Date from the ACOSA and Phillips Cooperative Studies

	ACOSA Study				Phillips Study			
	Athabasca		Lloydminster		California		Maya	
	ARC	WRI	ARC	WRI	ARC	WRI	ARC	WRI
Carbon (%)	83.55	83.17	83.07	83.80	83.16	84.35	83.96	85.40
Hydrogen (%)	10.49	10.56	11.12	11.12	11.33	11.75	11.10	11.55
Nitrogen (%)	0.45	0.52	0.33	0.42	0.74	0.75	0.38	0.40
Sulfur (%)	4.67 4.62[a]	4.61	3.79 3.80[a]	3.93	3.84	3.00	3.28	2.80
Relative Density (15°C/15°C)	1.005	1.005	0.971	0.971	0.945	0.942	0.943	0.940

[a]Data were generated by the Spectral Services Laboratory, University of Alberta, which frequently conducts these analyses for the Alberta Research Council.

These facts suggest that although a laboratory's data may contain a systematic error in relation to another laboratory at a single time, the magnitude of the error is not consistent. So one more variable, time, must be considered when judging the reliability of a single data point in a data base. This variable could be controlled by analysis of secondary standards.

4.3 Exchange of Oil Sand Samples

The exchange of samples of oil sand as described by the terms of the memorandum of understanding (MOU) pointed out another possible source of difference between the laboratories. There is no universal method for preparing test samples of bitumen from oil sand so each laboratory followed the method that it had developed for routinely examining oil sands.

4.3.1 Sample Collection and Preparation

The Athabasca oil sand analyzed in this exchange was sampled by the Alberta Research Council from the middle bench of the Suncor mining site near Fort McMurray in November 1976. The oil sand was stored in a freezer until April 1980 when it was thawed, manually homogenized, and repackaged in five 4.6-liter (1-gallon) metal cans each containing 7 kg (15 pounds). The contents of two of the containers were analyzed separately. Two other containers were sent to the Western Research Institute for analysis. In July 1980 about 11 to 16 kg (25 to 35 pounds) of tar sand material were collected by the Western Research Institute from the base of the cliff at the Uintah County quarry near Vernal, Utah. The cliff, an outcrop of the Asphalt Ridge tar sand deposit, is being actively used for paving material for county roads, parking lots, and driveways in the area. The material was reduced to chunks about 2.5 cm (1 inch) in diameter or less (the deposit is semiconsolidated to consolidated), exhaustively mixed, and packed into containers suitable for storage and shipping. Two of these containers each containing about 4 kg (9 pounds) were sent to the Alberta Research Council (ARC). Another of these containers was used as a source of tar sand material for the investigations at the Western Research Institute (WRI).

4.3.2 Determination of Bitumen, Water, and Solids Contents

One test sample of oil sand weighing approximately 120 g from each container was separated into bitumen, water, and solids at ARC by refluxing toluene in a Dean-Stark assembly for a period of 4 hours. The water was collected on phase-separating paper, weighed and mathematically corrected for water losses that routinely occur during reflux. The toluene extract was centrifuged for 2 hours at 960*g* to remove the fine solids. The solids in the extraction thimble and the centrifuged solids were dried in a forced-air oven and weighed. The toluene extract was transferred to aluminum trays and placed in a forced-air oven at 85°C (185°F) for 16 hours to remove the solvent.

Some types of bitumen are known to lose significant amounts of light materials during removal of the solvent in an oven. The total material balance for the Athabasca oil sand samples was 99%; the 1% loss was attributed to light ends. The Asphalt Ridge bitumen did not appear to lose a significant amount of light ends in the oven.

To obtain a more accurate bitumen figure for the Athabasca oil sand, the Dean-Stark extraction was repeated. After centrifuging, the toluene extract was diluted to a known volume. An aliquot was then pipetted onto a preweighed filter paper that was then placed in a fumehood. After a predetermined time in which the toluene is known to evaporate, the filter paper was again weighed to determine the weight of bitumen.[5] From this figure, the bitumen content of the oil sand was calculated. As expected, the measured bitumen content increased so a 100% material balance was obtained.

At WRI, approximately 175 g of tar sand (Athabasca or Asphalt Ridge) were extracted with toluene in a modified Soxhlet extractor for 24 hours or until the extracting solvent was colorless, which ever occurred last. In this extractor, the oil sand was held on a sintered-glass frit in the extractor. The water was removed from the toluene/bitumen/water solution by azeotropic distillation and measured in a Barrett receiver. The toluene/bitumen solution was vacuum-filtered through a 10- to 15-μm sintered glass funnel to remove traces of fine mineral matter. The toluene was removed using a rotary film evaporator and the bitumen was brought to constant weight. During solvent removal the overhead was monitored by gas chromatography to minimize loss of light ends.

The results from the two laboratories are compared in Table 4. The difference in water is attributed to the use of a correction factor in use at ARC at the time.[6] While this factor is appropriate for Athabasca oil sands, which usually contain greater than 2% water, it results in a correction of +0.2% for a water-free sample.

The higher bitumen content reported by WRI for the Asphalt Ridge oil sand was due to the high levels of solids in the bitumen. The average ash on ignition for the Asphalt Ridge bitumen samples was 0.92%; this corresponds to a solids content of approximately 1%. Agreement for the bitumen content of the Athabasca oil sand was much better because the ash content of the WRI bitumen samples was 0.2%.

4.3.3 Preparation of Test Samples of Bitumen

Two test samples of Athabasca bitumen, one from each container, and two of Asphalt Ridge bitumen were prepared at ARC by extracting one kilogram samples of oil sand held in cellulose thimbles with toluene in large Dean-Stark extractors. The extraction time was approximately 8 hours. The toluene extract was centrifuged at 960*g* to remove the fine solids. The solvent was then removed by rotary evaporation at 1 mm Hg and 40°C (104°F) to a level of less than 2%. The bitumen was stored in a refrigerator with minimum exposure to light before analysis.

At WRI, the ten bitumen samples from each deposit that had been isolated during the determination of bitumen content were combined to produce a total of five bitumen samples from each deposit. These bitumen samples, now a total of ten, were then used for all subsequent analyses. All of the bitumen samples were stored in a desiccator under nitrogen to minimize the possibility of oxidation of the bitumen samples. Each chemical and physical property was measured a minimum of five times, averaged, and the standard deviation of the data determined.

4.3.4 Comparison of Analyses

In this study, direct comparisons of elemental composition, average molecular weight, relative density (15°C/15°C), Ramsbottom carbon residue, nickel, vanadium, and compound classes were made. These results are given in

Table 4. Other tests, which were conducted by only one laboratory, will be discussed later.

Elemental Composition, Ash, and Molecular Weight: Elemental analyses of the bitumens prepared at the Alberta Research Council were carried out at the University of Alberta Spectral Services Laboratory. Carbon, hydrogen, and nitrogen were measured on a Perkin-Elmer 240B elemental analyzer and the level of sulfur by combustion in a Schöniger flask followed by titration. Oxygen values were determined by difference. The fact that the totals of carbon, hydrogen, nitrogen, and sulphur in all cases exceeded 99% indicated that the solids levels in the bitumen samples were low. Average molecular weights were determined by vapor pressure osmometry at the University of Alberta using benzene as the solvent. A single concentration of 2 mg/mL was used.

The ten samples prepared at WRI, five from each deposit, were submitted to a commercial analytical laboratory (Huffman Laboratories of Wheat Ridge, Colorado) for elemental analysis. The weight percentage of oxygen, as determined by the modified Unterzaucher method, appeared to be quite reliable for determining this element in these heavy fossil fuel samples.

Each sample was also ignited to constant weight. The average ash content for the Asphalt Ridge samples was 0.92% and the standard deviation of five tests was 0.45%. The Athabasca samples had a mean ash content of 0.20% and a standard deviation of 0.16%. The standard deviations were much higher than that caused by analytical error alone. The lack of precision was attributed to the utilization of sintered-glass funnels with questionable integrity. These funnels were used during the initial filtration, after bitumen extraction, to remove fine mineral matter.

The molecular weight of the bitumen samples was determined by Huffman Laboratories using vapor pressure osmometry with toluene as the solvent. The concentration of the sample varied between 2 and 47 mg/mL. The molecular weight of each of the ten samples was determined by extrapolating through three concentrations to infinite dilution.

If residual solids were the only cause of the differences in data between the two laboratories, the elemental analyses should have been almost identical for the Athabasca bitumen and the WRI results should have been consistently lower by approximately 1% for the Asphalt Ridge bitumen. But WRI reported higher results for sulfur, and lower results for carbon, hydrogen, and nitrogen. Clearly, either differences in the extraction methods or in the analyses caused the differing results. While it was not possible to examine the latter, it was thought that the longer extraction times employed by WRI may have resulted in more complete extraction of the organics from the oil sand. The difficult-to-remove organics presumably would be more polar or aromatic and contain more heteroatoms. The cellulose thimbles used at ARC could also selectively adsorb these types of compounds.

Table 4. Comparison of WRI and ARC Data from the Exchange of Oil Sands[a]

	Athabasca		Asphalt Ridge	
	ARC	WRI	ARC	WRI
Oil Sand Properties				
Bitumen (wt. %)	11.3, 11.4	10.8 (0.2)	9.9, 9.9	11.4 (0.4)
Solids (wt.%)	83.0, 83.1	–	89.5, 89.5	–
Water (wt.%)	5.7, 5.5	5.2 (0.4)	0.4, 0.4	<0.1
Bitumen Properties				
Carbon (%)	83.88, 83.84	83.17 (0.18)	86.46, 86.41	84.73 (0.39)
Hydrogen (%)	10.38, 10.60	10.34 (0.04)	11.84, 11.85	11.17 (0.08)
Nitrogen (%)	0.69, 0.73	0.41 (0.05)	0.87, 1.06	0.72 (0.03)
Oxygen (%)	0.79, 0.60 (by difference)	1.01 (0.15)	0.47, 0.19 (by difference)	1.73 (0.15)
Sulfur (%)	4.26, 4.23	5.01 (0.34)	0.36, 0.49	0.48 (0.03)
Average Mole. Wt. (daltons)	556, 579	525 (13)	458, 560	630 (8)
Relative Density (15°C/15°C)	1.012, 1.014	1.0161 (0.0017)	0.985	0.9986 (0.0067)
Chromatographic Separation				
SARA				
Saturates (%)	23.0	17.0 (1.0)	26.2	22.7 (3.3)
Aromatics (%)	13.2	24.9 (2.7)	6.9	13.5 (3.1)
Resins I (%)	37.6	35.5 (1.2)	35.0	32.6 (1.5)
Resins II (%)	8.9	6.6 (0.5)	25.6	20.4 (2.8)
Asphaltenes (%)	16.5	18.6 (0.4)	9.0	10.6 (2.2)
SAPA				
Saturates (%)	33.5	33.0 (1.5)	36.5	36.2 (0.6)
Aromatics (%)	36.1	35.2 (1.5)	24.4	25.6 (1.2)
Polar Aromatics (%)	15.4	14.2 (0.8)	32.9	28.7 (1.7)
Asphaltenes (%)	16.4	17.6 (0.5)	9.0	9.5 (1.0)
Ramsbottom Carbon Residue (%)	12.0, 11.8	12.40 (0.22)	8.96, 8.96	11.35 (0.95)
Metals (mg/kg)				
Nickel	66[b], 64[b] 67[c], 61[c]	52 (8)	52.5[b], 53.7[b] 53.4[c], 46.4[c]	60 (5)
Vanadium	211[b], 208[b] 159[c], 158[c]	211 (20)	6.7[b], 7.4[b] 3.5[c], 3.0[c]	18 (9)

[a]Standard deviations are reported in parentheses. For oil sand properties, the standard deviations were based upon ten determinations; for the remainder, five determinations were conducted.
[b]Ashing followed by AA at ARC.
[c]Ashing followed by ICP at a commercial laboratory.

Relative Density: Density measurements at ARC were taken on a density meter as described in ASTM D4052-81.[7] The densities were corrected for residual solvent concentration based upon the assumption that the volumes of mixing of toluene and bitumen are additive. The relative densities (15°C/15°C) reported in Table 4 were obtained by dividing the density of the sample at 15°C by the density of water at 15°C.

At WRI, relative density (15°C/15°C) was determined by ASTM D70-82, a pycnometer method.[8] This method is adaptable to moderate changes in temperature but not to changes in the pressure. However, it can be easily and inexpensively performed by all researchers. The relative densities of Athabasca bitumen at 15°C/15°C and 37.8°C/37.8°C were found by this method to be 1.0161 and 1.0045.

The two laboratories reported similar relative densities (15°C/15°C) for Athabasca bitumen but the WRI value of 0.9986 for Asphalt Ridge bitumen was higher than the ARC value of 0.985. This difference could not be attributed to the higher level of ash in the WRI samples. Mathematical correction for solids reduced the WRI value to 0.993.

The effect of sample preparation, therefore, was considered once more. While the longer extraction time employed by WRI may have led to a more complete extraction of the heavier polar compounds, the higher density also suggested that long exposure to heat and air under reflux could lead to the loss of lighter boiling components or conversion of some components to asphaltic structures.

Chromatographic Separations (SARA and SAPA): The SARA method involves the separation of bitumen into asphaltenes and maltenes followed by a chromatographic separation of the maltene fraction into four classes based upon adsorption on attapulgus clay and on silica.[5] The saturates and aromatics are eluted simultaneously with a nonpolar solvent from the attapulgus clay column. They are then separated on a silica column. The saturates usually contain very few heteroatoms. The aromatics contain some heteroatoms that are incorporated in high-molecular-weight compounds. The resin fractions that are eluted with more polar solvents from the clay column consist of molecules that contain actively available polar groups that do not precipitate with the asphaltene fraction.

It was observed that the within-laboratory precision of the SARA method was much poorer than that of the SAPA method, which is a separation on silica gel alone (see Table 4). The SARA method's lack of precision was attributed to the lack of quality control during production of the clay. It was observed that the extraction of the clay with the chromatographic solvents used in the SARA method resulted in the recovery of about 1% by weight of organic material from the clay. In addition, the clay as received was found to lose 1.8% of its weight (water) after heating overnight at 110°C (230°F) and an additional 3.4% of its weight (more water and undoubtedly organic material) after heating overnight at 482°C (900°F). Because of the above problems, neither laboratory now uses the SARA method for the separation of compound classes.

In the SAPA method, the maltene and n-pentane solution (minus asphaltenes) is concentrated to about 10 mL and placed on a water-jacketed column (100 x 2.5 cm) containing 140 g of Grace grade 62 silica gel.[9] The saturate fraction is eluted with 1 L of n-pentane, the aromatic fraction is eluted with 1 L of benzene, and the polar aromatic fraction is eluted with 1 to 1.5 L of benzene/methanol (9/1 by volume). Fractions are cut when the succeeding fraction is about 15 cm from the

bottom of the column. The solvent is removed from the aromatic and polar aromatic fractions using a rotary film evaporator. The fractions are dried to constant weight and weighed. The weight percentage of saturates was determined by difference at WRI and gravimetrically at ARC.

The saturate fraction that results from the SAPA method is usually pale yellow and darkens on exposure to the atmosphere, undoubtedly indicating the presence of some reactive compounds in this fraction. The small percentage of reactive material present in the saturate fraction can be eliminated by placing a small amount (10 to 20 g) of alumina at the bottom of the silica gel column. This method was originally intended as a simple means of comparing field-produced oil samples, rather than a method to separate tar sand bitumen into discrete compound classes. Proton NMR confirmed the presence of aromatic hydrogens in most of the saturate fractions produced by the two separations.

The solvents and adsorbents used to separate the maltenes into components varied between the SARA and the SAPA methods, resulting in different estimates of the proportion of saturates and aromatics in the samples, but the method of asphaltene precipitation was fixed. The asphaltenes were precipitated by first dissolving the bitumen in an equal volume of benzene and then treating the solution with 40 volumes (mL) of pentane to one weight (g) of bitumen. The asphaltenes were collected by filtration and washed with pentane until the washings were colorless.

ARC's estimates of asphaltene content were lower than the WRI estimates. Differences in sample preparation were again identified as a possible cause of the analytical variation.

The elemental compositions of the fractions from the SARA and SAPA separations are given in Tables 5 and 6. The compositions reported by ARC and WRI for fractions from the SAPA method were similar except for the determination of oxygen. This was also true for the fractions from the SARA method. Due to problems associated with the SARA method, the number of significant differences in the SARA data was greater. The standard deviations reported for the fractions were usually greater than the standard deviations determined for the analysis of these elements in the original bitumen samples. This, however, reflected nothing more than the combination of two sources of error — that associated with elemental analysis and that associated with chromatographic separation.

The elemental compositions of the original bitumens were calculated from the proportions and compositions of the fractions using the WRI data to assess the consistency of the elemental analyses (Table 7). This estimate of the original elemental composition was not as good for the SARA chromatographic method as it was for the SAPA method. The calculated weight percentages of carbon and oxygen deviated significantly from the values obtained by direct measurements. The discrepancies were believed due primarily to water in the tetrahydrofuran remaining in the resins II fraction from the SARA method. The water could not be removed even by repeated benzene azeotropic distillation.

Calculation of the elemental composition of the whole bitumens from the composition of the fractions using the ARC data was less than satisfactory, partially because the compositions were based on one analysis of each fraction. ARC also had more severe problems with water retention in the resins II fraction from the SARA method and methanol retention in the polar aromatics fraction from the SAPA method.

Ramsbottom Carbon Residue: Ramsbottom carbon percentages were determined by ASTM D524-81.[10] The high standard deviation calculated for the Asphalt Ridge samples at WRI was believed to have been caused in part by the high and erratic ash percentages. The cause of these high and erratic ash percentages was discussed earlier. Subtracting the previously determined ash percentages and recalculating the Ramsbottom carbon data resulted in the following information:

Athabasca – 12.20 wt. percent (s = 0.25)

Asphalt Ridge – 10.43 wt. percent (s = 0.57)

These corrected data agreed well with ARC's data for the Athabasca bitumen (11.9% RCR) but not for Asphalt Ridge bitumen (8.96% RCR). Differences in sample preparation were again considered to be a possible cause.

Nickel and Vanadium: Test samples of the bitumen extracted at ARC were ashed and the residue dissolved in acid before the nickel and vanadium were measured by atomic absorption. The sample preparation procedure was duplicated at a commercial laboratory before the sample was analyzed by inductively coupled argon plasma. The commercial laboratory and ARC's measurement of vanadium differed by as much as a factor of two. The reason is not known.

WRI followed a colorimetric method developed by Bean to determine the nickel and vanadium content.[11] In this method, the presence of iron can contribute to high values for vanadium. The discrepancy between the ARC and WRI vanadium values was greater for the Asphalt Ridge samples than for the Athabasca samples. This was attributed to higher levels of solids, and therefore iron, in the Asphalt Ridge samples.

Table 5. Elemental Composition of Fractions Collected from the SARA Method[a]

	Carbon	Hydrogen	Weight % Nitrogen	Oxygen[b]	Sulfur	Average Mole. Wt. (daltons)	H/C Atomic Ratio
Athabasca Bitumen							
Saturates							
ARC	86.74	13.05	0.00	0.64	0.48	380	1.81
WRI	86.29	13.49	<0.10	0.12	0.12	352	1.88
	(0.34)	(0.04)		(0.02)	(0.03)		
Aromatics							
ARC	85.84	10.34	0.00	0.63	4.19	360	1.44
WRI	85.18	10.45	<0.10	0.19	4.11	365	1.47
	(0.22)	(0.09)		(0.14)	(0.38)		
Resins I							
ARC	81.96	9.55	0.51	2.45	5.75	743	1.40
WRI	80.94	9.68	0.58	2.83	5.82	646	1.44
	(0.25)	(0.10)	(0.04)	(0.14)	(0.33)		
Resins II							
ARC	71.51	9.15	0.72	14.39	3.39	397	1.54
WRI	69.62	9.59	0.30	18.59	1.05	462	1.65
Asphaltenes							
ARC	80.44	8.09	1.22	2.31	8.71	4698	1.21
WRI[c]	79.81	8.26	1.09	2.27	8.51	3135	1.24
	(0.51)	(0.09)	(0.07)	(0.29)	(0.69)		
Asphalt Ridge Bitumen							
Saturates							
ARC	86.25	13.25	0.16	0.65	0.10	458	1.84
WRI	86.46	13.20	0.14	0.14	0.11	424	1.83
	(0.25)	(0.25)	(0.08)	(0.10)	(0.02)		
Aromatics							
ARC	88.94	10.74	0.00	0.29	0.77	369	1.45
WRI	88.21	11.10	0.10	0.19	0.43	391	1.51
	(0.34)	(0.15)	(0.00)	(0.13)	(0.08)		
Resins I							
ARC	85.86	10.62	0.97	2.43	0.80	882	1.48
WRI	84.06	10.74	1.07	3.28	0.66	774	1.53
	(0.58)	(0.18)	(0.10)	(0.70)	(0.04)		
Resins II							
ARC	77.01	9.21	1.17	10.91	1.75	651	1.44
WRI	79.09	10.42	1.17	8.84	0.40	1527,	1.58
	(3.25)	(0.22)	(0.19)	(3.77)	(0.16)	883	
Asphaltenes							
ARC	83.84	9.36	1.90	3.91	0.89	4547	1.34
WRI[c]	83.77	9.58	1.86	3.80	0.99	3070	1.37
	(0.75)	(0.20)	(0.11)	(0.80)	(0.45)		

[a] The standard deviations reported by WRI for five samples are given in parentheses.
[b] The ARC estimates of oxygen content were obtained by difference.
[c] Data were normalized as the solids entrained in the bitumen were concentrated in the asphaltene fraction.

Table 6. Elemental Composition of Fractions Collected from the SAPA Method[a]

	Weight %						
	Carbon	Hydrogen	Nitrogen	Oxygen[b]	Sulfur	Average Mole. Wt. (daltons)	H/C Atomic Ratio
Athabasca Bitumen							
Saturates							
ARC	86.43	12.46	0.33	0.33	1.26	353	1.73
WRI	86.22	12.36	<0.10	0.22	1.47	359	1.72
	(0.22)	(0.14)		(0.10)	(0.19)	(6)	
Aromatics							
ARC	83.14	9.64	0.38	1.42	6.06	546	1.39
WRI	82.81	9.62	0.46	0.89	5.83	569	1.39
	(0.40)	(0.06)	(0.16)	(0.22)	(0.14)	(16)	
Polar Aromatics							
ARC	75.98	9.89	0.68	8.22	5.99	847	1.56
WRI	78.30	9.90	0.68	4.09	6.35	787	1.52
	(0.47)	(0.31)	(0.16)	(0.28)	(0.30)	(55)	
Asphaltenes							
ARC	80.44	8.09	1.22	2.31	8.71	4698	1.21
WRI[c]	80.57	8.22	1.09	2.17	7.95	3162	1.22
	(0.21)	(0.22)	(0.07)	(0.20)	(0.27)	(237)	
Asphalt Ridge Bitumen							
Saturates							
ARC	86.51	12.81	0.12	0.44	0.21	397	1.78
WRI	86.84	12.47	<0.10	0.19	0.20	446	1.72
	(0.41)	(0.25)		(0.09)	(0.03)	(19)	
Aromatics							
ARC	85.92	10.24	0.61	2.44	0.72	553	1.43
WRI	86.35	10.59	0.88	1.51	0.41	762	1.47
	(0.63)	(0.13)	(0.15)	(0.41)	(0.07)	(105)	
Polar Aromatics							
ARC	83.20	10.35	1.32	4.66	1.08	1107	1.49
WRI	82.95	10.61	1.32	3.52	1.08	1219	1.53
	(0.32)	(0.09)	(0.12)	(0.16)	(0.27)	(19)	
Asphaltenes							
ARC	83.84	9.36	1.90	3.91	0.89	4547	1.34
WRI[c]	83.31	9.60	1.93	4.35	0.81	2832	1.38
	(0.67)	(0.13)	(0.15)	(0.72)	(0.39)	(366)	

[a] The standard deviations reported by WRI for five samples are given in parentheses.
[b] The ARC estimates of oxygen content were obtained by difference.
[c] Data were normalized as the solids entrained in the bitumen were concentrated in the asphaltene fraction.

Table 7. **Calculation of the Elemental Composition of Bitumen from the Composition of its Fractions**

	Weight %				
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
ARC Data					
Athabasca Bitumen					
Measured	83.84	10.60	0.73	0.60	4.23
Calculated (SARA)	81.98	10.14	0.46	2.85	4.58
Calculated (SAPA)	82.34	10.31	0.54	2.23	4.87
Asphalt Ridge Bitumen					
Measured	86.41	11.85	1.06	0.19	0.49
Calculated (SARA)	83.46	10.80	0.83	4.06	0.86
Calculated (SAPA)	84.90	11.09	0.78	2.56	0.67
WRI Data					
Athabasca Bitumen					
Measured	83.17	10.34	0.41	1.01	5.01
Calculated (SARA)	82.01	10.24	0.46	2.65	4.64
Calculated (SAPA)	82.99	10.33	0.48	1.35	4.85
Asphalt Ridge Bitumen					
Measured	84.73	11.17	0.72	1.73	0.48
Calculated (SARA)	84.18	11.17	0.83	3.34	0.48
Calculated (SAPA)	85.52	11.21	0.82	1.89	0.56

4.3.5 Other Properties of Oil Sand

Because the bitumen in Athabasca oil sand is currently being extracted commercially using the hot-water process, ARC has adopted as part of its assessment of oil sands, determinations of water-soluble salts and particle-size distribution. Both factors influence the conditions that should be established for bitumen extraction and the percentage of the bitumen that can be recovered.

To determine the level of water-soluble salts, 50 g of the oil sand samples were extracted with an equal weight of hot distilled water. The water extracts were analyzed after purification by centrifugation and filtration through a 0.45-μm Millipore filter. Studies carried out after this work was completed showed that some fine particles may pass through a 0.45-μm filter and may be measured as soluble salts.[9] A 0.1-μm filter is now used. The cations were measured by atomic absorption and the anions by ion chromatography.

The ions in the water extract are ions that are present not only in the connate water but as salts deposited in the formation. The concentrations of the ions as shown in Table 8 represent parts per million of the oil sand by weight. Sulfate and soluble calcium and magnesium are produced in oil sand during storage at a rate dependent upon the storage temperature. The values reported, therefore, may not be representative of the formation.

Table 8. Water-Soluble Salts in Athabasca and Asphalt Ridge Oil Sands

	Athabasca A	Athabasca B	Asphalt Ridge A	Asphalt Ridge B
Cations (ppm by wt.)				
Calcium	20	20	30	45
Iron	0.20	0.07	0.3	0.2
Magnesium	10.5	10.3	3.5	6.0
Manganese	0.04	0.04	0.05	0.06
Potassium	8.8	8.4	0.8	1.3
Sodium	14.3	13.1	1.0	1.5
Anions (ppm by wt.)				
Chloride	2.7	0.9	0.7	5.0
Fluoride	1.0	0.8	0.2	0.3
Nitrate	2.6	1.0	ND	ND
Sulfate	81	83	84	119
pH	7.7	8.1	6.1	6.6
Conductivity (mmho/cm)	0.30	0.30	0.22	0.30

ND - none detected

The particle-size distribution of the dried solids was determined by the Oil Sands Research Department of ARC by sieving followed by Coulter counter measurements on the <37.2-μm fraction. For comparison, samples of oil sand were submitted to the Geological Survey Department of ARC where they were extracted with toluene in a cellulose thimble and the size distribution of the extracted solids was measured. An X-ray sedigraph was used to measure the distribution in the <44-μm fraction.

The difference in the results (Table 9) was attributed to the fact that the Geological Survey Department dispersed the solids in water before sieving while the Oil Sands Research Department used isopropyl alcohol. The statistical parameters reported in Table 10 clearly illustrate the fact that water is a stronger dispersing agent for the clays than isopropyl alcohol. The Geological Survey results consistently showed a smaller mean and median grain size and indicated a stronger skewness in the direction of the fine fractions.

The two analytical procedures used to determine the particle-size distribution reflect the concerns of the individuals who use such data. The Geological Survey Department is interested in geological sedimentation and needs complete dispersion of the particles. Therefore, that department has adopted a procedure whereby the sample is dispersed in water so the clay lumps and cemented sand grains are broken into individual particles as much as possible. In the Oil Sands Research Department there is more concern with the engineering aspects of oil sand. In many processes, the lumps of clay in oil sand are not broken up. Therefore, when characterizing oil sand, the sample is dispersed in isopropyl alcohol so the lumps are not completely disaggregated.

Table 9. Cumulative Particle-Size Distributions of Oil Sand Solids

Particle Size		Athabasca A		Athabasca B		Asphalt Ridge A		Asphalt Ridge B	
Ø	μm	OSRD	Geol. Survey	OSRD	Geol. Survey	OSRD	Geol. Survey	OSRD	Geol. Survey
-0.50	1414	–	0.05	–	0.07	–	0.04	–	–
0.00	1000	2.04	0.08	2.42	0.10	0.17	0.05	0.13	–
0.50	707	2.73	0.21	2.86	0.28	0.65	0.19	0.48	0.10
1.00	500	3.86	0.46	3.95	0.63	4.06	1.79	4.48	1.63
1.50	354	4.98	0.80	5.43	1.04	19.21	14.19	19.53	14.30
2.00	250	11.56	3.92	12.41	3.74	51.67	40.21	51.63	41.22
2.50	177	30.54	25.23	32.88	22.95	75.36	66.40	74.69	69.65
3.00	125	54.02	48.78	57.12	45.98	86.72	78.60	85.27	82.37
3.50	88.4	77.70	71.60	80.82	69.73	93.14	86.90	92.01	89.37
4.00	62.5	85.06	81.32	87.92	79.26	95.46	92.06	94.65	93.27
4.50	44.2	89.81	83.91	92.50	81.91	97.30	93.73	96.61	94.56
4.75	37.2	90.87	84.35	93.56	82.54	97.76	94.22	97.6	94.97
5.00	31.3	–	84.79	–	83.17	–	94.70	–	95.37
5.50	22.1	91.2	86.12	93.7	85.07	98.9	96.15	98.2	96.40
6.00	15.6	91.5	87.49	93.8	86.79	99.3	96.58	98.6	97.09
6.50	11.1	92.4	88.89	94.3	88.41	99.7	97.28	99.3	97.63
7.00	7.8	92.8	90.22	94.7	89.72	99.8	97.81	99.5	98.04
7.50	5.5	93.7	91.47	95.7	90.99	100.0	98.18	99.8	98.42
8.00	3.9	94.2	92.80	96.2	92.40	–	98.65	99.9	98.72
8.50	2.8	95.4	93.93	97.4	93.67	–	98.91	100.0	98.99
9.00	2.0	96.2	95.01	97.9	94.85	–	99.16	–	99.22
9.50	1.4	98.4	95.98	99.0	95.94	–	99.37	–	99.43
10.00	0.98	99.2	96.87	99.5	96.75	–	99.53	–	99.54
10.50	0.69	100.0	97.51	100.0	97.38	–	99.60	–	99.59
11.00	0.49	–	97.99	–	98.01	–	99.72	–	99.73
12.00	0.24	–	100.00	–	100.00	–	100.00	–	100.00

Table 10. Statistical Parameters Relating to Particle-Size Distribution

Statistical Parameters	Asphalt Ridge A		Asphalt Ridge B		Athabasca A		Athabasca B	
	OSRD	Geol. Survey	OSRD	Geol. Survey	OSRD	Geol. Survey	OSRD	Geol. Survey
Median Grain Size (Ø)	2.914	3.027	2.853	3.085	1.974	2.187	1.975	2.154
(μm)	132.7	122.7	138.4	117.8	254.5	219.6	254.4	224.7
Mean Grain Size (Ø)	2.986	3.287	2.888	3.540	2.083	2.349	2.099	2.267
(μm)	126.2	102.5	135.1	86.0	236.0	196.3	233.4	207.8
Description of Average Grain Size	fine sand	very fine sand	fine sand	very fine sand	fine sand	fine sand	fine sand	fine sand
Graphic Std. Deviation (Ø)	0.906	1.134	0.818	1.450	0.743	0.895	0.779	0.792
Inclusive Std. Deviation (Ø)	1.487	1.624	1.286	1.792	0.806	1.052	0.855	0.947
Description of Sorting	poorly sorted	poorly sorted	poorly sorted	poorly sorted	moderately sorted	poorly sorted	moderately sorted	moderately sorted
Graphic Skewness	0.119	0.344	0.064	0.476	0.219	0.272	0.240	0.214
Inclusive Graphic Skewness	0.357	0.526	0.275	0.589	0.281	0.371	0.308	0.326
Description of Skewness	fine skewed	strongly fine skewed	fine skewed	strongly fine skewed	fine skewed	strongly fine skewed	strongly fine skewed	strongly fine skewed
Measure of Kurtosis	2.568	2.421	2.222	2.327	1.302	1.429	1.355	1.472
Description of Kurtosis	very lepto-kurtic	very lepto-kurtic	very lepto-kurtic	very lepto-kurtic	lepto-kurtic	lepto-kurtic	lepto-kurtic	lepto-kurtic

4.3.6 Other Properties of Bitumen

Researchers at WRI routinely determine the weight percentage of wax in tar sand bitumen samples because of its effect on the oil recovered from in situ thermal recovery projects in Utah. High concentrations of wax and associated high pour points in produced oil can result in the plugging of production flow lines if the flow lines are not maintained at a temperature above the pour point of the oil. For example, the bitumen in the zone where WRI's first field project (TS-1C) was conducted, contained about 28% wax and had a pour point of 66°C (150°F). Other selected samples from this same zone contained up to 85% wax and had a pour point of about 93°C (199°F).[12]

The average pour point data and weight percentages of wax as determined by WRI are given in Table 11. The pour points of the bitumen samples were determined using ASTM D97-66.[13] The wax percentages of the bitumen samples were determined by dissolving 1 g of bitumen in 3.75 g of toluene, adding 11.25 g of methyl ethyl ketone, and stirring at -20°C (-4°F) for 2 hours. The wax was collected in a tared 10- to 15-μm sintered-glass funnel, washed twice with 25 mL of cold methyl ethyl ketone, dried, and weighed.

Researchers at ARC have not generally considered Athabasca bitumen to be waxy because the saturates from the chromatographic separations are liquid rather than solid at ambient temperatures.They have chosen to measure viscosity to determine the heat required to induce movement of bitumen in a formation and to prevent clogging of production lines.

Table 11. Pour Point and Wax Determinations of the Bitumen Samples[a]

	Pour Point		Wax
	(°C)	(°F)	(%)
Athabasca	28 (2)	82 (3)	8.6 (1.1)
Asphalt Ridge	45 (2)	113 (4)	17.0 (1.1)

[a] Standard deviations of five determinations are reported in parentheses.

The viscosity of bitumen is extremely sensitive to even small amounts of residual solvent. A method developed by Shu appears to provide a reasonable correction for residual solvent levels up to 10%.[14] A formula proposed by Cragoe cannot be used above 1.5% solvent.[15] Neither formula provides corrections when measurements of viscosity are made above the boiling point of the pure solvent.

An alternative to making a mathematical correction for residual solvent entails complete removal of the solvent during sample preparation. This strategy, however, often requires extreme conditions that also remove the light components of the bitumen. Removal of solvent to a predetermined level is also not feasible as the viscosity of the crude defines the conditions required. The variations that can be expected even within one laboratory as a result of the residual solvent problem can be seen in the data collected by ARC (Table 12) using a Brookfield cone and plate viscometer.[16] The solvent level was reduced in all cases under what was thought to be the same conditions of rotary evaporation.

Table 12. Absolute Viscosity of the Bitumen Samples[a]

	Athabasca A	Athabasca B	Asphalt Ridge A	Asphalt Ridge B
Temperature				
65°C (149°F)	1918	1604	7680	16910
107°C (225°F)	196	154	451	539
150°C (302°F)	41	35	77	82
% Solvent	1.28	1.85	1.93	0.02

[a] Viscosities are reported in centipoise.

Both ARC and WRI performed simulated distillations on their samples of bitumen but the output was in a format that could not be compared. At ARC, the simulated distillations were carried out on a Perkin-Elmer 3B gas chromatograph. The column dimensions were 1.8 m (6 ft) L x 1.6 mm (1/16")I.D. It was packed with 10% OV-1 on Chromosorb Q. The conditions of the distillation were set such that the resolution between the C_{16} and C_{18} internal standard peaks was approximately four. The results of the distillations at ARC are given in Table 13. The percentages reported are volume percent.

Table 13. Simulated Distillation Data for Athabasca and Asphalt Ridge Bitumens by ARC

Cut Temp	°C	(°F)	Volume % Distilled Athabasca A	Athabasca B	Asphalt Ridge A	Asphalt Ridge B
IBP			165°C (229°F)	168°C (335°F)	139°C (282°F)	146°C (295°F)
Naphtha	175	(347)	0.6	0.4	0.6	0.4
	195	(383)	0.8	0.7	0.5	0.3
	225	(437)	1.2	1.4	1.0	0.7
	250	(482)	2.3	1.9	1.3	1.0
Light gas oil	275	(527)	3.4	4.3	1.9	1.7
	300	(572)	4.5	4.9	2.3	2.1
	325	(617)	5.6	6.1	2.9	2.6
	343	(649)	4.6	4.8	2.3	2.3
Heavy gas oil	375	(707)	8.6	8.8	4.1	4.1
plus residue	400	(752)	6.6	6.8	3.8	3.7
	>400	(>752)	61.6	59.7	78.6	80.5

The WRI method yielded data in weight percentage of material distilling in 56°C (100°F) increments (Table 14). Consequently, it is difficult to compare data directly. However, comparisons can be made by plotting the data and estimating the percentage of material distilling in different temperature increments. Results from cooperative studies indicate there is no significant difference between volume and weight percentage data.[1]

The WRI simulated distillation calculations are based on the use of an external standard (shale oil distillate) in preference to an internal standard (four n-alkanes) to determine the response factor. The use of the simulated distillation method as described here has resulted in a good comparison between tar sand bitumen data obtained according to the Hempel distillation method.[17]

Table 14. Simulated Distillation Data for Athabasca and Asphalt Ridge Bitumens by WRI[a]

	Weight Percentage of Distillable Material in the Range, °C (°F)							
	149-204 (300-400)	204-260 (400-500)	260-316 (500-600)	316-371 (600-700)	371-427 (700-800)	427-482 (800-900)	482-538 (900-1000)	Residue
Athabasca	0.1 (0.1)	1.6(0.4)	5.4(0.2)	9.1 (0.2)	10.4(0.3)	10.5(0.4)	8.8(0.4)	54.1(0.9)
Asphalt Ridge	0.1 (0.1)	1.0(0.3)	3.5(0.2)	6.2(0.1)	7.8(0.3)	12.2(0.4)	9.9(0.3)	59.3(0.5)

[a] Standard deviation of five determinations are reported in parentheses.

5. CONTRIBUTION OF SAMPLE PREPARATION TO VARIABILITY IN ANALYTICAL DATA

5.1 Background

In the previous chapter, differences in the methods of extracting test samples of bitumen from oil sand were identified as a possible source of discrepancy between analytical data from WRI and ARC. This chapter describes the work carried out at ARC to evaluate the effect of sample preparation on selected properties of Athabasca and Asphalt Ridge bitumen.

5.2 Experimental Design

In the original exchange of oil sand samples, both laboratories had used a method based upon the continuous refluxing of hot toluene, but thimble types, extraction times, and solids removal procedures varied considerably. At ARC the oil sand was held in a cellulose thimble. At WRI it was held in place by a sintered-glass frit in the reflux apparatus. At ARC extractions were carried out only until the toluene extract became colorless (approximately 3 hours). At WRI the extraction was continued for a minimum of 24 hours. The asphaltene, carbon residue, and density data in Table 4 suggest that the ARC method could result in either incomplete extraction of the bitumen from the oil sand or adsorption of polar components on the cellulose thimble. On the other hand it is possible that the long extraction time at WRI could cause formation of asphaltenic components in the extraction flask.

During extraction, fine solids in oil sand tend to pass into the bitumen extract. These are routinely removed by centrifugation at ARC and by filtration through a sintered-glass funnel at WRI. A comparison of the efficiencies of these procedures was incorporated into the study to determine if the efficiency of solids removal could have contributed to the differences reported in Table 15.

A series of bitumen samples was extracted using a combination of the extraction conditions summarized in Table 16. This pattern was adopted to fulfill the requirements of a factorial design, the approach chosen for this study. A discussion of factorial experiments follows in 5.3.

Table 15. Summary of the Major Differences in Data from the 1980 Sample Exchange

	Athabasca		Asphalt Ridge	
	ARC	WRI	ARC	WRI
Carbon (%)	83.86	83.17	86.44	84.73
Asphaltenes (%)	16.5	18.1	9.0	10.1
Ramsbottom Carbon Residue (%)	11.9	12.4	9.0	11.4
Relative Density (15°C/15°C)	1.013	1.016	0.985	0.999

Table 16. Experimental Conditions for the Extraction of Bitumen from Oil Sand

Trial	Extraction Time (x_1)	Thimble Type (x_2)	Solids Removal (x_3)
1	short	wire	centrifugation
2	long	wire	centrifugation
3	short	paper	centrifugation
4	long	paper	centrifugation
5	short	wire	filtration
6	long	wire	filtration
7	short	paper	filtration
8	long	paper	filtration

The short extraction times given in Table 16 were the minimum times plus one hour required to obtain a colorless extract from the oil sand as determined in preliminary experiments. For the Athabasca sample, a 3-hour extraction was appropriate and for the Asphalt Ridge, 24 hours were required. (In this study, the Asphalt Ridge oil sand was considerably more consolidated and required a much longer extraction time to obtain a colorless extract than in the original exchange.) The long extraction times were set at 24 and 48 hours for the Athabasca and Asphalt Ridge samples, respectively.

The thimbles used to hold the oil sand were either Whatman cellulose thimbles (13 cm L x 4 cm I.D.) or wire thimbles of the same dimensions and constructed of 325-mesh stainless steel. Glass thimbles fitted with sintered-glass frits were not used because of their tendency to plug, resulting in decreased flow of solvent through the oil sand. This alteration of the original WRI method is not expected to have affected the results. Fine solids in the bitumen extract were removed either by ultra centrifugation at 9000*g* for one hour or vacuum filtration through a sintered-glass filter (medium frit, 10 to 15 μm).

All trials listed in Table 16 were duplicated in random order to preserve the integrity of the statistical analyses. Solvent was removed by rotary evaporation, first at 60°C (140°F) and 15 mm Hg for 1 hour and then at 60°C (140°F) and 1 mm Hg for 4 hours. These conditions resulted in residual solvent levels of less than 0.5% for Athabasca bitumen and usually less than 2.5% for Asphalt Ridge bitumen.

The following methods were used to determine the properties of the bitumen samples:

% Ash	Ignition to constant weight at 538°C (1000°F)
Viscosity	ASTM D3205-79 (Brookfield cone and plate viscometer) [16]
Density	A modification of ASTM D71-78 in which methanol is the displaced fluid [18]
Elemental Carbon	Perkin Elmer 240B CHN analyzer
Asphaltenes	Syncrude analytical method 5.1 (precipitation of a 40:1:1 mixture of pentane:sample:benzene followed by filtration through a sintered-glass filter with a medium frit) [5]
Ramsbottom Carbon Residue	ASTM D524-81 [10]

5.3 Design and Interpretation of Factorial Experiments [19]

Either a classical or a statistical strategy can be followed when examining the effect of several variables or factors on the results of an experiment.

In the classical approach, all of the factors except one are held constant, that factor is varied, and its effect on the results is determined. Experiments are then repeated for a second factor and so on, until all have been examined. The following assumptions are implicit in the one-factor-at-a-time approach. First, the response is likely to be a complicated function of each factor and, therefore, many experiments are required. Second, the factors do not interact. In other words, if two factors are changed simultaneously the overall effect equals the sum of the effects when those same factors are changed one at a time. Third, experimental error is negligible compared with the effects of changing the factor levels.

In the statistical approach it is assumed that the response functions are either linear or have only a slight upward or downward curvature, interactions between factors are typical, and experimental error may be significant. These assumptions are reasonable for the examination of the effect of extraction conditions on properties of the extracted bitumen.

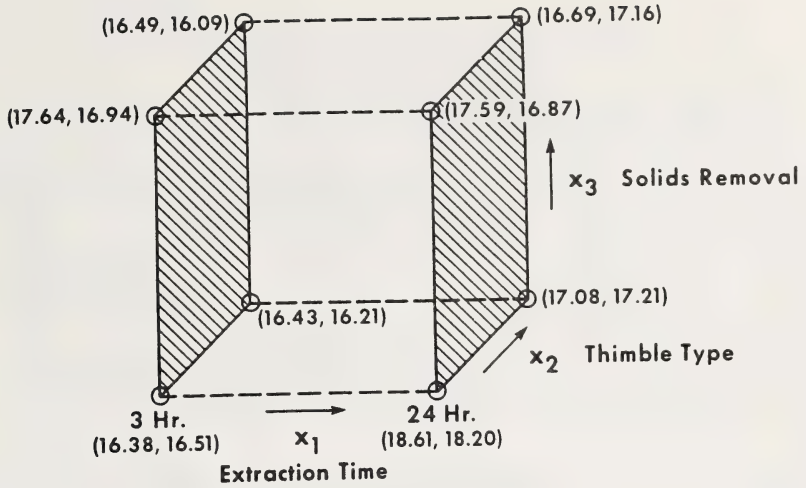
In a factorial experiment the significance of varying a factor is determined by comparing the average of the results from all experiments in which the level of the factor was maximized with the results in which the level was minimized. For this study, in which only three factors were examined, the experiment can be represented as a cube, as shown in Figure 2a, 2b, and 2c. The effect of changing a factor is the difference between the mean results on the opposite faces of the cube.

In the statistical analyses the significance of the effect is determined with the repeatabilities of the experiments taken into account. As an example, analysis of the data presented in Figure 2 is given in Table 17. When data in the columns show an effect greater than the minimum significant effect, this means the factors or interactions associated with those columns are significant.

For example, in Table 17, the average asphaltene content of bitumens extracted for 24 hours is shown to be 17.4% whereas the average asphaltene content of bitumen extracted for 3 hours is shown to be 16.6%. The average difference of 0.8% is judged to be significant at the 95% level of confidence because it exceeds the minimum significant value of 0.37%.

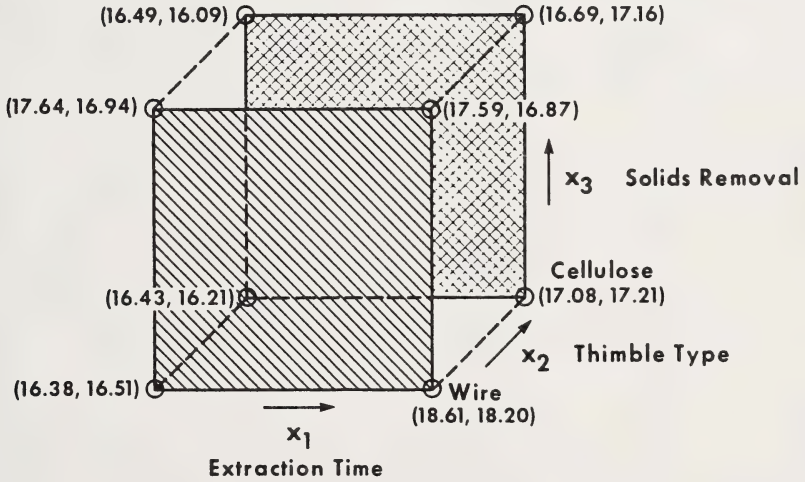
On the other hand, bitumen that was extracted from oil sand held in a paper thimble contained significantly less asphaltenes than that extracted from oil sand held in a wire thimble. The negative value of the effect denotes that as one changes from the negative level (wire) to the positive level (paper) a decrease in the measured value occurs. The method of solids removal had no significant effect at the 95% level of confidence.

Interactions are considerably more difficult to interpret. For example, with an x_1x_3 (extraction time-solids removal) interaction, the assumption may be made that by increasing the extraction time, an organic material only slightly soluble in toluene is extracted. If this extra material adsorbs on the glass frit of a sintered-glass funnel, but is not removed by centrifugation, an interaction is said to have occurred. This case is presented as an example only and may not in fact represent what has really happened. In this study interactions between factors are probably not as crucial as the effect of the individual factors. Therefore, they are not discussed extensively.



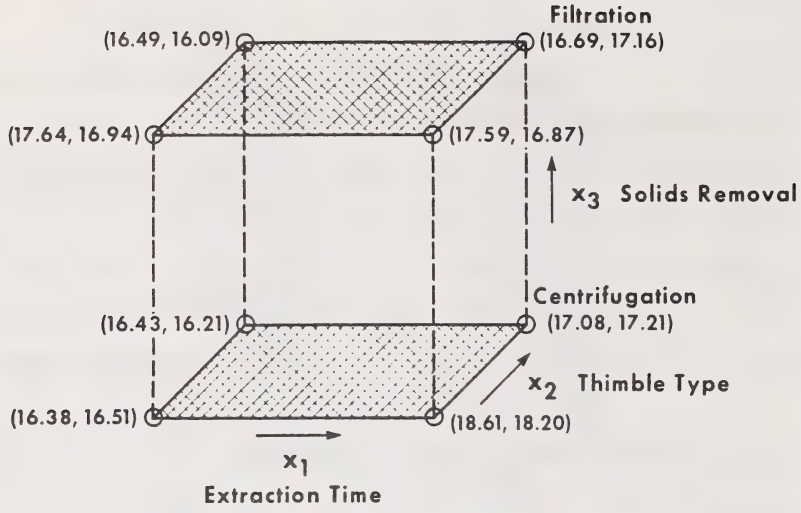
3 Hr. -- $\bar{x}$ = 16.59%
24 Hr. -- $\bar{x}$ = 17.43%
Average Difference -- 0.84%

Figure 2a Representation of the Effect of Extraction Time on the Percentage of Asphaltenes in Athabasca Bitumen



Wire -- $\bar{x}$ = 17.34%
Cellulose -- $\bar{x}$ = 16.67%
Average Difference -- 0.67%

Figure 2b Representation of the Effect of Thimble Type on the Percentage of Asphaltenes in Athabasca Bitumen



Centrifugation -- $\bar{x}$ = 17.08%
Filtration -- $\bar{x}$ = 16.93%
Average Difference -- 0.15%

Figure 2c Representation of the Effect of Solids Removal Method on the Percentage of Asphaltenes in Athabasca Bitumen

Table 17. Example of the Computation of Factor Effects from a Two-Level Design Using Percentage of Asphaltenes in Athabasca Bitumen

		Extraction Time	Thimble Type		Solids Removal				Asphaltenes (%)			
Trial	Mean	x_1	x_2	x_1x_2	x_3	x_1x_3	x_2x_3	$x_1x_2x_3$	(1)	(2)	$\bar{x}$	s
1	+	-	-	+	-	+	+	-	16.38	16.52	16.45	0.0990
2	+	+	-	-	-	-	+	+	18.61	18.20	18.41	0.2899
3	+	-	+	-	-	+	-	+	16.43	16.21	16.32	0.1556
4	+	+	+	+	-	-	-	-	17.08	17.22	17.15	0.0990
5	+	-	-	+	+	-	-	+	17.64	16.94	17.29	0.4950
6	+	+	-	-	+	+	-	-	17.59	16.87	17.23	0.5091
7	+	-	+	-	+	-	+	-	16.49	16.09	16.29	0.2828
8	+	+	+	+	+	+	+	+	16.69	17.16	16.93	0.3323
Ave +		17.43	16.67	16.96	16.94	16.73	17.02	17.24				
Ave -		16.59	17.35	17.06	17.08	17.29	17.00	16.78				
Effect		0.84	-0.68	-0.10	-0.14	-0.56	0.02	0.46				

$s_{pooled} = 0.32$

Minimum significant effect at the 95% level of confidence $= ts \times \sqrt{2/mk}$

$= 2.31 \times 0.32 \times \sqrt{2/(4 \times 2)} = 0.37$

t Student's "t" value

m number of trials/2

k number of replicates per trial

Experimental Coding

+ : 24-hr. extraction, paper thimbles, filtration

- : 3-hr. extraction, wire thimbles, centrifugation

5.4 Results and Discussion

The original data, including residual solvent content and residue (ash) upon ignition, collected in this study are listed in Tables 18 and 19. The elemental carbon, asphaltenes, carbon residue and density values were, however, corrected for both contaminants before they were entered in the statistical calculations. Viscosity was originally thought to be sensitive to slight changes in the proportion of heavy fractions in bitumen. Therefore, viscosity data, corrected for residual solvent, was also statistically evaluated. The formulae for correcting the data were

1. Asphaltenes

$$\text{Corrected \% Asphaltenes} = \frac{100 \times (\%\ \text{Asphaltenes}_{\text{Meas}} - \%\ \text{Solids})}{100 - \%\ \text{Solids} - \%\ \text{Toluene}}$$

2. Ramsbottom Carbon Residue (RCR)

$$\text{Corrected \% RCR} = \frac{100 \times (\%\ \text{RCR}_{\text{Meas}} - \%\ \text{Ash})}{100 - \%\ \text{Solids} - \%\ \text{Toluene}}$$

3. Elemental Carbon

$$\text{Corrected \% Carbon} = \frac{100 \times (\%\ \text{Carbon}_{\text{Meas}} - [0.9125 \times \%\ \text{Toluene}])}{100 - \%\ \text{Solids} - \%\ \text{Toluene}}$$

where 0.9125 is the fraction of carbon in toluene

4. Relative Density (15°C/15°C)

$$\text{Corrected Density (15°C)} = \frac{100 - \%\ \text{Solids} - \%\ \text{Toluene}}{\frac{100}{\text{Density}_{\text{Meas}}\ (15°\text{C})} - \frac{\%\ \text{Solids}}{2.5} - \frac{\%\ \text{Toluene}}{0.8669}}$$

where 2.5 and 0.8669 are the densities of solids and toluene

$$\text{Relative Density (15°C/15°C)} = \frac{\text{Density}_{\text{Corr}}\ (15°\text{C})}{\text{Density}_{\text{Water}}\ (15°\text{C})}$$

5. Viscosity on a solvent-free basis

Viscosities were corrected for residual solvent using the equation of Shu.[14] Here, a parameter α is defined and incorporated into the classical Arrhenius expression that relates the viscosity of a mixture to the viscosity of its components:

$$\alpha = \frac{17.04\,\Delta p^{0.5237}\,\rho_{Bitumen}^{3.2745}\,\rho_{Toluene}^{1.6316}}{\ln\frac{\mu_{Bitumen}}{\mu_{Tolvene}}} \quad (1)$$

$$x_{Bitumen} = \frac{\alpha V_{Bitumen}}{\alpha V_{Bitumen} + V_{Toluene}} \quad (2)$$

$$x_{Toluene} = 1 - x_{Bitumen} \quad (3)$$

and

$$\ln\mu_{Mixture} = x_{Bitumen}\ln\mu_{Bitumen} + x_{Toluene}\ln\mu_{Toluene} \quad (4)$$

Where ρ = density (15°C)
μ = viscosity (cp)
V = volume fraction
x = volume fraction adjusted for α

A first approximation for α is obtained by substituting measured density values and an estimate of the viscosity of the pure bitumen into equation 1. $x_{Bitumen}$ and $x_{Toluene}$ are then calculated and substituted into the Arrhenius equation, which is solved for viscosity of the pure bitumen. If the calculated value is significantly different than the value used to estimate α, the new value for $\mu_{Bitumen}$ is used to determine a new value for α. The process is repeated until a constant $\mu_{Bitumen}$ is achieved. This correction assumes that light ends are not lost during the removal of solvent.

Compared with the levels in the original exchange, the ash after ignition of the Asphalt Ridge bitumen samples was quite high. The fines that contributed to the ash had probably been produced when the oil sand was milled and homogenized before extraction. Although centrifugation is a more efficient method than filtration of removing fines, the levels of fines in the centrifuged Asphalt Ridge bitumen samples were much higher than those found in Athabasca bitumen samples prepared in a similar manner. It is believed that the Asphalt Ridge fines did not adhere to the bottom of the centrifuge tube when the bitumen-toluene mixture was decanted.

Because the ash level was so high, the test sample weight in the analyses had to be corrected for the original solids. The magnitude of corrections is apparent in Tables 18 and 19. Subsequent ashing to constant weight at 538°C (1000°F) of fines recovered by centrifuging revealed that the solids from Athabasca bitumen lost 8% of their weight when ashed. The solids from Asphalt Ridge bitumen lost 18% of their weight when ashed.

Table 18. Properties of Athabasca Bitumen Extracted Under Various Conditions

	Experimental Data								Corrected Data				
Trial	Solids (%)	Ash (%)	Toluene (%)	Relative Density (15°C/15°C)	Viscosity (cp at 60°C)	Carbon (%)	Asphaltenes (%)	RCR (%)	Relative Density (15°C/15°C)	Viscosity (cp at 60°C)	Carbon (%)	Asphaltenes (%)	RCR (%)
1	0.45	0.42	0.34	1.0038	2150	84.13	16.70	12.4	1.0016	2290	84.49	16.38	12.09
	0.29	0.27	0.14	1.0025	3430	83.58	16.74	11.7	1.0010	3530	83.81	16.52	11.48
2	0.33	0.31	0.00	0.9916	4250	83.59	18.88	12.2	0.9896	4250	83.87	18.61	11.93
	0.26	0.24	0.06	1.0057	3780	83.53	18.40	12.2	1.0043	3820	83.74	18.20	12.00
3	0.14	0.13	0.18	0.9955	3330	83.85	16.52	12.0	0.9949	3460	83.95	16.43	11.91
	0.16	0.15	0.04	1.0027	4550	83.76	16.34	11.9	1.0018	4590	83.89	16.21	11.77
4	0.22	0.20	0.00	1.0003	3400	83.84	17.26	12.1	0.9990	3400	84.02	17.08	11.93
	0.19	0.18	0.08	1.0035	4200	83.90	17.37	12.4	1.0025	4250	84.06	17.22	12.25
5	0.30	0.28	0.42	1.0044	5040	83.94	17.81	12.4	1.0032	5510	84.16	17.64	12.21
	0.22	0.20	0.07	1.0053	4690	83.19	17.11	12.0	1.0041	4760	83.36	16.94	11.83
6	0.33	0.31	0.03	1.0055	3860	83.71	17.86	12.2	1.0036	3880	83.99	17.59	11.93
	0.40	0.37	0.00	1.0065	3620	83.85	17.20	12.2	1.0040	3620	84.19	16.87	11.88
7	0.41	0.38	0.04	1.0085	4560	83.39	16.82	12.3	1.0061	4600	83.73	16.49	11.97
	0.17	0.16	0.12	1.0008	3340	83.81	16.22	11.4	1.0000	3420	83.95	16.09	11.27
8	0.17	0.16	0.00	1.0009	3250	83.85	16.83	11.9	0.9999	3250	84.00	16.69	11.76
	0.16	0.15	0.00	0.9999	3740	83.63	17.29	12.0	0.9989	3740	83.77	17.16	11.87

Table 19. Properties of Asphalt Ridge Bitumen Extracted Under Various Conditions

	Experimental Data								Corrected Data				
Trial	Solids (%)	Ash (%)	Toluene (%)	Relative Density (15°C/ 15°C)	Viscosity (cp at 60°C)	Carbon (%)	Asphaltenes (%)	RCR (%)	Relative Density (15°C/ 15°C)	Viscosity (cp at 60°C)	Carbon (%)	Asphaltenes (%)	RCR (%)
1	1.44	1.22	4.07	0.9875	15,500	85.26	9.67	10.0	0.9843	64,400	86.30	8.71	9.29
	4.20	3.56	1.33	0.9849	22,500	82.99	11.47	12.1	0.9609	35,300	86.56	7.69	9.04
2	0.25	0.21	1.50	0.9948	24,800	86.35	9.30	9.5	0.9955	40,300	86.49	9.21	9.46
	1.30	1.10	1.44	0.9890	24,200	84.91	9.31	10.2	0.9831	39,100	85.95	8.24	9.36
3	2.25	1.91	1.38	0.9863	24,200	84.93	10.23	10.9	0.9745	38,800	86.83	8.27	9.33
	1.68	1.42	2.49	0.9751	16,200	84.89	9.16	10.6	0.9680	40,200	86.21	7.81	9.58
4	0.14	0.12	1.48	0.9662	19,000	87.01	7.86	8.8	0.9671	33,400	87.07	7.85	8.82
	0.05	0.04	1.29	0.9760	24,800	86.72	8.33	9.1	0.9773	39,800	86.70	8.40	9.18
5	6.07	5.14	1.81	1.0092	20,900	81.67	14.13	14.0	0.9741	35,300	86.86	8.75	9.62
	5.95	5.04	1.94	1.0136	15,100	81.82	13.98	13.8	0.9795	25,400	86.90	8.72	9.51
6	6.63	5.62	2.08	1.0000	19,000	80.50	14.90	14.4	0.9614	36,000	86.10	9.06	9.62
	8.02	6.80	1.91	1.0216	20,600	79.79	15.37	15.5	0.9740	34,400	86.66	8.16	9.66
7	2.67	2.26	1.31	0.9735	23,000	84.42	9.61	10.7	0.9588	37,400	86.67	7.23	8.79
	3.74	3.17	2.46	0.9877	13,700	83.45	11.08	11.9	0.9679	30,200	86.57	7.83	9.31
8	3.06	2.59	1.38	0.9763	25,700	83.77	10.92	11.5	0.9593	43,300	86.34	8.23	9.32
	1.29	1.09	2.64	0.9866	13,900	85.26	9.24	10.3	0.9824	33,000	86.24	8.28	9.59

Only the asphaltene content was significantly affected when the three factors were changed during sample preparation (Tables 20 and 21). Increasing the extraction time from 3 to 24 hours caused an increase of 1% in asphaltene content of Athabasca bitumen. Paper thimbles in place of wire thimbles caused a reduction in asphaltene content of 0.7 and 0.6% for the Athabasca and Asphalt Ridge samples.

Table 20. Identification of Significant Factors During the Extraction of Athabasca Bitumen

	Increasing Extraction Time from 3 to 24 hours (x_1)	Changing from Wire to Paper Thimbles (x_2)	Changing from Centrifugation to Filtration to Remove Solids (x_3)	Minimum Significant Effect (95% level of confidence)
Ash (%)	-0.01	-0.11	-0.01	0.09
Relative Density (15°C/15°C)	0.0013	-0.0010	0.0032	0.0051
Viscosity (cp at 60°C)	-242	-122	402	706
Elemental Carbon (%)	0.04	-0.03	-0.09	0.32
Asphaltenes (%)	0.84	-0.67	-0.15	0.37
Ramsbottom Carbon Residue (%)	0.13	-0.08	-0.08	0.31

Table 21. Identification of Significant Factors During the Extraction of Asphalt Ridge Bitumen

	Increasing Extraction Time from 3 to 24 hours (x_1)	Changing from Wire to Paper Thimbles (x_2)	Changing from Centrifugation to Filtration to Remove Solids (x_3)	Minimum Significant Effect (95% level of confidence)
Ash (%)	-0.75	-2.06	2.72	1.06
Relative Density (15°C/15°C)	0.0040	-0.0072	-0.0067	0.0102
Viscosity (cp at 60°C)	-1350	-2150	2100	10544
Elemental Carbon (%)	-0.17	0.10	0.03	0.32
Asphaltenes	0.30	-0.58	0.01	0.55
Ramsbottom Carbon Residue (%)	0.07	-0.21	0.17	0.23

Several of the test samples prepared at ARC were analyzed at WRI to determine if good agreement could be obtained. The comparisons (corrected for residual solvent and solids) showed that equivalent elemental carbon values were obtained on single test samples of bitumen (Table 22). The differences in the two laboratories' asphaltene data were probably caused by differences in test methods. Obtaining agreement for a method-defined property such as asphaltenes is

unlikely to occur because most organizations have probably developed empirical correlations based upon their own data and methods and are unlikely to change.[20]

Table 22. Comparison of Analyses by WRI and ARC of Bitumens Prepared in the Factorial Experiments[a]

	Carbon (%)		Carbon Residue (%)		Asphaltenes (%)	
	ARC	WRI	ARC (RCR)	WRI (CCR)	ARC	WRI
Athabasca						
Trial 7A	83.73	83.94	12.0	12.0	16.5	19.1
Trial 8A	84.00	83.54	11.8	12.1	16.7	19.1
Trial 1B	83.81	83.73	11.5	12.1	16.5	19.0
Trial 7B	83.95	84.03	11.3	12.3	16.1	20.3
$\bar{x}$	83.87	83.81	11.7	12.1	16.5	19.4
Asphalt Ridge						
Trial 3B	86.21	85.91	9.6	9.3	7.8	10.8
Trial 6A	86.10	86.10	9.6	8.5	9.1	8.3
Trial 2B	85.95	85.34	9.4	9.6	8.2	12.0
Trial 6B	86.66	86.37	9.7	9.0	8.2	9.3
$\bar{x}$	86.23	85.93	9.6	9.1	8.3	10.1

[a] All data were corrected for solids and residual solvent.

By the time these samples were analyzed, WRI was using a Conradson carbon residue (CCR) test[21] in place of a Ramsbottom carbon residue (RCR) test.[10] The ASTM correlation chart suggests that at 10% RCR, CCR values should be approximately 12%. Based on this correlation ARC's RCR values were roughly equivalent to WRI's CCR values. However, it must be realized that this is an approximate correlation of empirical properties based on petroleum products and not on oil sand bitumens. Thus, the correlation may not be valid.

As a result of the factorial experiment, more samples of bitumen were extracted at ARC to determine if an increase in extraction time affected asphaltene recovery. The Asphalt Ridge oil sand used in this study was ground to pass a 100-micron sieve so that an extraction time of 3 hours was sufficient to produce a colorless extract. Extra precautions were taken when decanting the Asphalt Ridge extract after centrifugation to hold the level of ash to less than 1.5%. Asphaltene content, which had been shown to be the only property that could be used to detect the effect of different sample preparation methods, was corrected for residual solvent and solids in all of the samples (Table 23).

Table 23. Confirmation of the Factorial Experiments[a]

Method of Sample Preparation	Asphaltenes (%)			
	Athabasca		Asphalt Ridge	
	$\bar{x}$	s	$\bar{x}$	s
A. Paper thimbles; 3-hour extraction	16.77	0.19	6.53	0.26
B. Paper thimbles; 3-hour extraction; extract boiled for an additional 21 hours	17.28	0.17	–	–
C. Paper thimbles; 3-hour extraction; sand removed and the thimble extracted for 21 hours	17.79	0.33	6.77	0.87
D. Paper thimbles; 24-hour extraction	17.18	0.14	6.21	0.58

[a] All values represent measurements on four samples.

In this set of extractions an increase in extraction time from 3 to 24 hours did not significantly increase the asphaltene content of Asphalt Ridge bitumen (compare A with D). However, boiling the bitumen-toluene solution extracted from Athabasca oil sand caused an increase in asphaltene content of 0.5% (compare A with B) and a further 0.5% increase resulted from extracting the emptied thimble for 21 hours (compare B with C). This indicates that asphaltenes can be produced from Athabasca bitumen during long extraction times. In addition, asphaltenes can adsorb on cellulose thimbles. Extraction of the thimble with its contents for the full 24 hours resulted in the same asphaltene content as the samples that were extracted for 3 hours and from which the extract alone was boiled for an additional 21 hours (B and D). This is attributed to the presence of sand, which reduces the volume of solvent passing through the thimble. Thus, less efficient extraction of the thimble would result. The reader is directed to the reference to Speight et al.[20] for further detailed discussions of this subject.

Given the data in Tables 20 and 21 which show only asphaltene content is affected by the method of bitumen extraction and the data in Table 22 which show this effect is sometimes minor, it is concluded therefore that the physical and chemical properties of bitumen are changed only to a minor extent during routine extraction. Most of the differences resulting from the original ARC-WRI sample exchange arose from an inability by both laboratories at the time to make proper corrections for entrained solids and residual solvent and differences in analytical methods.

6. CONCLUSIONS FROM LABORATORY STUDIES

1. It has been shown that the Alberta Research Council and the Western Research Institute can obtain good agreement on a majority of the properties determined on exchanged samples. The determination of only one property is still in question; that is the determination of asphaltenes. Unfortunately, there are at least eight standard procedures available to perform this determination[20] and it is believed that each laboratory will continue to use their method of choice.

2. It has also been shown that to obtain good agreement of data between laboratories strict attention to detail is necessary. For example, variations in the method of bitumen extraction and purification can have a significant effect on the measured properties of the bitumen. Corrections for residual solvent and solids are crucial for elemental carbon, carbon residue, asphaltenes, viscosity, and density determinations.

3. A single method for preparing a test sample of bitumen cannot be applied to all oil sands. The method developed at ARC for Athabasca bitumen yielded bitumen with levels of solids and solvent that would be excessive for Asphalt Ridge bitumen. The long extraction times required to extract bitumen completely from Asphalt Ridge oil sand could cause chemical changes. Thus, this procedure would be inappropriate for Athabasca bitumen. Paper thimbles used to hold oil sand in the extractors adsorb some of the asphaltene fraction but not enough of that fraction to significantly affect other properties of bitumen.

4. The evaluation of literature data can only be accomplished if detailed methods are included. If this type of information is not available then the data can only be used for the generation of typical or average values.

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Peter Flach formerly of the Alberta Research Council and Donna Sinks formerly of the Western Research Institute prepared Appendices A and B.

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APPENDIX A GEOLOGICAL DESCRIPTION OF THE ATHABASCA DEPOSIT

1. Geological Setting

The Athabasca oil sand deposit is contained predominantly within the Lower Cretaceous McMurray Formation, which unconformably overlies the Devonian Beaverhill Lake Formation and is comformably overlain by the Clearwater Formation. The formations are basically undisturbed tectonically. Local faulting may be present, caused by the dissolution of underlying Devonian evaporites and the subsequent collapse of overlying strata.

2. Nature of Oil-Bearing Zone

The McMurray Formation can be divided into three informal members, a lower, a middle and an upper member. Throughout most of the deposit, the middle and upper members (top 55 m (180 ft.) or so) are entirely oil bearing wherever there is sufficient porosity and permeability for the bitumen to have entered the sand. There are rare, thin gas zones near the top of the formation and zones that once contained gas but are now water bearing. The lower member of the McMurray Formation can be oil bearing, but is often water bearing, especially in the lows on the Devonian limestone surface.

The McMurray Formation varies in thickness from 0 m at the pinchout edge in the west to over 120 m (400 ft.) in some of the small collapse features in the center of the deposit. The gross pay thickness is about the same as the average thickness of the formation, 55 m (180 ft.). The net pay is a sum of all the rich (>10%) saturated oil sands in the formation, whether or not the pay section is interrupted by shale beds.

Oil saturation of the sands is up to 18% oil by weight, with 14 to 16% being common in the channel sands. Average saturation is approximately 9%.

3. Aerial Extent of Oil-Bearing Zones and Reservoir Continuity

Most of the rich oil sands sections of the McMurray Formation are found in fluvial channel deposits. This type of sedimentation results in the highly discontinuous nature of the oil sand bodies. Correlation is often difficult or impossible, even over a distance of a hundred metres.

Deposits which are laterally more continuous are found in the upper member of the formation. These marine deposits, however, are not commonly well developed.

4. Lithology

Sands in the McMurray Formation are quartzose with a small amount of feldspar grains. Richly saturated fluvial channel sands generally have very low clay contents, less then 1.5%. The sands are usually very fine- to fine-grained but medium- and coarse-grained sands are present in the lower portions of the formation.

5. Overburden

The overburden in the Athabasca oil sands area varies from 0 m along the Athabasca River valley, where the McMurray Formation outcrops, to approximately 600 m (2000 ft.) in the southwest portion of the deposit.

Clearwater formation shales and sands directly overlie the McMurray Formation over most of its aerial extent. In the surface mineable area, i.e. <45 m (150 ft.) of overburden, glacial deposits may directly overlie the McMurray Formation as well.

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APPENDIX B GEOLOGICAL DESCRIPTION OF THE ASPHALT RIDGE DEPOSIT

1. Geological Setting

The major oil-impregnated strata at the Asphalt Ridge deposit occur in the Rimrock Formation of the Mesaverde Group of late Cretaceous Age and the Oligocene Duchesne River Formation (Tertiary). The Asphalt Ridge is a 10-km (15-mile)-long, northwest-trending cuesta on the northeastern edge of the Uinta Basin. At Asphalt Ridge oil-impregnated strata are exposed along the entire strike of the ridge. About 35 m (115 ft.) of saturated Rimrock Formation are exposed at the northwest end of the ridge, while 60 m (190 ft.) of oil-bearing Duchesne River Formation are exposed at the Uintah County asphalt quarry. These two formations are separated by an erosional unconformity. At Asphalt Ridge dips of the Rimrock Formation range from 12-28° southwest, while the Duchesne River Formation is less steep, dipping about 5-20°. A 275-m (900-ft.) displacement fault significantly lowered the northwest end of the ridge. The faulting in the area occurred before deposition of the Tertiary strata.

2. Lithology

The Rimrock Formation is a highly saturated, semi-consolidated to consolidated, fine- to medium-grained sandstone with many low-saturated claystone, siltstone, and shale intervals. The sediments are of near shore marine origin. The sandstone contains 60% chert, 37% quartz, and minor accessory minerals and is commonly cemented by calcite. Most chert grains are subangular, while the quartz is generally subrounded.

The Duchesne River Formation formed in a fluvial-deltaic environment, thus causing the wide range in grain size and sorting of the sediments. It is characterized by interbedded, poorly sorted sandstones, red to grey shale of Paleozoic age. The Uinta Mountains to the north were the source for some of the coarser sediments.

3. Nature of the Oil-Bearing Formations

Analyses of samples from the Rimrock and Duchesne River formations indicate variations in porosity, permeability, and oil and water saturations. Both formations are classified as oil-wet. Porosities of the Rimrock Formation range from 26-34% (average of saturated zones), while the Duchesne River Formation has lower average porosity, ranging from 18-29%. Saturated permeabilities vary considerably from 1-170 md. for both formations. Oil saturation values average about 8 wt.% in the Rimrock Formation. The Duchesne River Formation has slightly lower average oil saturation values of about 6-7 wt.%. Values of water saturation vary randomly from 1% to 8 wt.%.

4. **Source of Oil**

The oil in the Cretaceous and Oligocene strata probably originated in the lacustrine Green River Formation oil shales of the Uinta Basin. During tectonic activity the sediments of the Asphalt Ridge area were uplifted in relation to those of the Uinta Basin, allowing the oils of the Eocene sediments to migrate updip along the porous and permeable sandstones near the unconformity. Faulting also contributed to localizing the migrating oils, forming impermeable barriers, thus creating structural traps. Migration of the oil occurred post-Oligocene time following deposition of the Duchesne River Formation.

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APPENDIX C COMPOSITE DESCRIPTION OF A TYPICAL ATHABASCA OIL SAND SAMPLE

Sample History[1]

Classification: Oil Sand
Country: Canada
Field: Athabasca
Stratigraphic Unit: McMurray
Location: Sec 23, TWP 92, Rge 10, W4M
Method of Production: Mining
Depth: 40 m
Source: Suncor Inc., Fort McMurray, Alberta
Sample Date: November 1981

Properties of Whole Oil Sand [1]

Bitumen (wt.%)	14.6
Water (wt.%)	1.1
Mineral (wt.%)	84.1

Visual and Petrologic Description [2,3]

The sample is an oil-rich, fine-grained sand that is moderately well sorted. Quartz makes up 90 to 95% of the mineral. The quartz grains are mainly subangular to subrounded although a smaller number of well-rounded grains are present. They are mainly monocrystalline; very few polycrystalline quartz grains are present. A small percentage of the quartz grains possess euhedral and abraded overgrowths.

Cryptocrystalline rock fragments, mainly chert, microcline, orthoclase, muscovite, tourmaline, and zircon are the most important accessory minerals in the sand-sized fraction. They comprise about 2% of the total mineral content.

The most abundant clay minerals are kaolinite and illite (identified by X-ray diffraction). Minor quantities of chlorite, vermiculite and smectite are also present. Scanning electron microscope studies revealed the presence of small quantities of authigenic kaolinite as hexagonally shaped booklets or as clay bridges between the quartz grains.

The sample shows little evidence of compaction or other diagenetic effects. The quartz grains are weakly cemented by heavy oil and there is evidence of only very local carbonate cementation. Small amounts of diagenetic minerals such as pyrite, marcasite, and siderite occur in nodules throughout the sample.

Sand Mineralogy

Major: quartz
Minor: chert, muscovite
Trace: zircon, pyrite, marcasite, siderite, microcline, orthoclase, tourmaline

Clay Mineralogy

Major: kaolinite, illite
Minor: chlorite, vermiculite, smectite

Cementation

Weak heavy oil cementation throughout and local carbonate cementation

Grain Size Distribution (1)

Ø	Wt% Retained
0	0.6
0.5	0.6
1.0	3.7
1.5	9.5
2.0	30.8
2.5	39.9
3.0	7.0
3.5	2.5
4.0	0.9
4.5	1.1
4.75	0.1
>4.75	3.3

Median (Ø)	2.061
Graphic mean (Ø)	2.025
Inclusive standard deviation (Ø)	0.652
Graphic skewness	-0.113
Inclusive graphic skewness	0.055
Graphic kurtosis	1.588

Water Soluble Salts (mg/kg of oil sand)

Na	5.3
Ca	0.8
Mg	0.2
Fe	0.4
Cl	2.4
HCO_3	0.0
SO_4	8.0
CO_3	0.0

Hydrocarbon Characteristics	
Gravity (°API)	8.9
Relative Density (15°C/15°C)	1.008
Viscosity (cp)	
15°C (59°F)	1,011,600
25°C (77°F)	265,300
60°C (140°F)	4,620
100°C (212°F)	114
Average Mole. Wt. (daltons)	521
Carbon Residue (RCR) (%)	12.0
Ash (%)	0.10
Carbon (%)	83.48
Hydrogen (%)	10.30
Nitrogen (%)	0.47
Sulfur (%)	4.20
Oxygen (%)	1.50
Vanadium (ppm wt.)	204.2
Nickel (ppm wt.)	81.0
Saturates (%)	24.4
Aromatics (%)	13.5
Resins I (%)	36.7
Resins II (%)	6.3
Asphaltenes (%)	17.2
Acid Number (mg KOH/g bitumen)	2.72
Heat of Combustion (kJ/kg)	41,660

Distillation Cut Temp. °C	(°F)	Vol.%	Cumulative Vol.%
123	(254)	IBP	0.5
150	(302)	0.5	1.0
175	(347)	0.7	1.7
195	(383)	0.8	2.5
225	(437)	0.7	3.2
250	(482)	0.8	4.0
275	(527)	0.8	4.8
300	(572)	2.7	7.5
325	(617)	3.0	10.5
343	(649)	3.5	14.0
375	(707)	7.0	21.0
400	(752)	5.0	26.0
425	(797)	3.5	29.5
450	(842)	10.5	40.0
475	(887)	7.5	47.5
500	(932)	10.5	58.0
524	(975)	11.0	69.0
Residue		31.0	100.0

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